Cross-linked poly(arylene ether ketone) membranes sulfonated on both backbone and pendant position for high proton conduction and low water uptake

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HIGHLIGHTS

► Cross-linked PAEK membranes sulfonated on both backbone and pendant position were prepared.
► Cross-linked PAEK membranes with DS above 120% exhibited higher proton conductivity than Nafion®117.
► Methanol permeability and water uptake were maintained still very low, compared to Nafion®117.
► Properties of membrane were correlated with ionic cluster dimension measured by SAXS.

ARTICLE INFO

ABSTRACT

A series of cross-linkable poly(arylene ether ketone)s (PAEKs) with sulfonic acid groups on both the backbone and pendant positions are synthesized through direct condensation polymerization. The degree of sulfonation (DS) of the polymer backbone is controlled by changing the feed ratios of sulfonated to unsulfonated monomers. Post-polymerization reactions are successfully employed to prepare polymer electrolyte membranes for fuel cell applications. The chemical structures of the synthesized polymers are confirmed by ^{1}H nuclear magnetic resonance (NMR) and Fourier transform infrared (FT-IR) spectroscopy. The thermal and mechanical properties of the membranes are character-ized by thermogravimetric analysis and stress–strain test. The dependence of water uptake, methanol permeability, proton conductivity, and selectivity on DS is studied. The cross-linked sulfonated PAEK (CSPAEK) membranes with DS higher than 120% exhibit higher proton conductivity than those of Nafion® 117. The CSPAEK membranes maintain very low methanol permeability and water uptake. The properties of all the membrane are correlated with ionic cluster dimension measured by small angle X-ray scat-tering (SAXS).

1. Introduction

Interest has recently increased in the development of new polymer electrolyte membranes (PEMs) for fuel cells, as PEM is one of the most important components in the fuel cell system. The key required features of high performance proton exchange membranes include: (1) high conductivity, (2) low methanol permeability, (3) low water uptake, (4) good mechanical properties, (5) low cost, and (6) feasible membrane electrode assembly fabrication [1,2]. The most widely used commercial membrane is Nafion® due to its high proton conductivity and excellent chemical and mechanical prop-erties [3]. However, Nafion® membranes have some drawbacks such as high methanol permeability, high cost, and low operating temperature [1,4]. For these reasons, extensive research efforts have been conducted to find suitable alternatives to Nafion® membranes such as sulfonated poly(arylene ether ketone) (SPAEK), sulfonated poly(benzimidazoles), sulfonated poly(sulfone), and sulfonated poly(ether amide) [5–20].

Among these polymers, SPAEK has emerged as a promising candidate with great potential for practical uses due to its excellent physical properties [21–28]. SPAEKs are usually prepared either by post-sulfonation of commercially available polymers or by direct copolymerization of sulfonated monomers. Post-sulfonation method has been widely used because of the relatively simple reaction procedure in comparison with direct copolymerization method. However, precisely controlling the degree of sulfonation (DS), which is defined as the number of sulfonic acid groups (−SO₃H groups) per repeating unit, in the post-sulfonating proce-dure is quite difficult [29–32]. The preparation of membranes with

accurately controlled chemical structures from monomers has thus been considered an effective approach for establishing a well-defined DS and the desired properties [12,33–35].

Wang et al. [36] found that the polymers with pendant sulfonic acid groups are more stable to hydrolysis than those with sulfonic acid groups directly attached on the polymer (aryl) backbone. Therefore, the physical and chemical stability of the cross-linked SPAEK (CSPAEK) membranes can be controlled by appropriately balancing the number of sulfonic acid groups attached on the polymer backbone and that of the pendant positions, as well as by changing DS. In order to increase the proton conductivity to maintain high thermal, mechanical, and hydrolytic resistance, not only the backbone (aryl) but also the pendant sulfonation may be a good trial.

For sulfonated polymer membranes in general, both the proton conductivity and water uptake increase simultaneously with increasing DS. The membranes with excessively high DS frequently suffer problems associated with excessively high water uptake and thus poor dimensional and mechanical stability during the fuel cell operation [37,38]. Cross-linking is one of the most comprehensive approaches for solving these problems. However, the results have consistently shown that the increased cross-linking density reduces proton conductivity of the PEM [39,40]. Recent evidence also suggests that if the degree of cross-linking (DC) is too high, the polymer membrane becomes too brittle with low toughness [41,42]. One way to avoid reducing the proton conductivity by cross-linking is to use a cross-linker that contains the proton conducting moiety, i.e., sulfonic acid. In our previous work, a series of CSPAEK membranes was successfully synthesized based on this idea [43]. The membranes prepared exhibited low methanol permeability and excellent thermal and mechanical properties, but the proton conductivity remained too low to be a true alternative to Nafion®.

In this study, SPAEK was first synthesized via direct copolymerization of backbone sulfonated and unsulfonated monomers. Post-polymerization reactions were used to produce a series of cross-linkable SPAEKs. The pendant sulfonation and cross-linking reactions were carried out at the same time. The cross-linking reaction forms amide bonds between the activated carboxylic acid groups of PAEKs and the amine groups of cross-linkers, as the amide groups are the most stable in all the carbonyl functional groups due to their high resonance stabilization between the nitrogen–carbon and carbon–oxygen bonds [44]. The cross-linking density was controlled by the content of sulfonic acid-containing cross-linker, 4,4′-diamino-2,2′-biphenyl disulfonic acid. After post-polymerization, the prepared membranes were expected to show high proton conductivity but low water uptake and methanol permeability when the DS of the backbone and pendant position and DC were appropriately controlled.

2. Experimental

2.1. Materials

2,2′-benzidine disulfonic acid (BDSA) was obtained from Tokyo Chemical Industry (TCI, Japan). 4,4-bis(4-hydroxyphenyl)-valeric acid, 4,4′-difluorobenzophenone, potassium carbonate (K_2CO_3), dimethyl sulfoxide (DMSO), toluene, N,N′-dicyclohexylcarbodiimide (DCC), N-hydroxysuccinimide (NHS), dimethylformamide (DMF), N,N-dimethyl acetamide (DMAc), hydrochloric acid (HCl), sodium hydroxide (NaOH), methanol, isopropanol, fuming sulfuric acid 30% SO_3, sodium sulfanilate, and tetrahydrofuran (THF) were purchased from Aldrich (Aldrich, USA) and used directly.

Table 1
Monomer feed ratio and basic chemical structure of CSPAEK membranes synthesized.

Sample	m (mol)	n (mol)	DC (%)	DS (%)
CSPAEK0	0.0100	0	15	100
CSPAEK10	0.0090	0.0010	15	120
CSPAEK15	0.0085	0.0015	15	130
CSPAEK20	0.0080	0.0020	15	140
CSPAEK25	0.0075	0.0025	15	150
CSPAEK30	0.0070	0.0030	15	160
CSPAEK35	0.0065	0.0035	15	170
CSPAEK40	0.0060	0.0040	15	180

m: moles of 4,4′-difluorobenzophenone fed; n: moles of 5,5′-carbonylbis(2-fluorobenzene-sulfonate) fed; DC: degree of cross-linking; DS: degree of sulfonation.

2.2. Synthesis of SPAEK

Sodium 5,5′-carbonylbis(2-fluorobenzene-sulfonate) (S-Ketone) was first synthesized according to the procedure described by Wang et al. [33]. The pure sulfonated monomer was obtained after the product was re-crystallized twice in distilled water and dried in a vacuum oven at 80 °C for 24 h. Yield: 14 g (92%).

Fourier transform infrared (FT-IR) spectroscopy (KBr, cm^{-1}) 1026, 1084, 1240 (O=S=O); 1700 (C=O), ^{1}H nuclear magnetic resonance (NMR) (DMSO-d6, ppm) 1, 7.3; 2, 7.7; 3, 8.1.

In the experiment, SPAEKs were synthesized directly from three different monomers: 4,4-bis(4-hydroxyphenyl)-valeric acid, 4,4-difluoro benzophenone as an unsulfonated monomer and 5,5-carbonylbis(2-fluorobenzene-sulfonate) as a sulfonated monomer. Sulfonated polymers with exact DS were ideally controlled by simply adjusting the feed ratio of sulfonated and unsulfonated monomers. As a detailed example, SPAEK20 was synthesized as follows. Dry DMSO (45 g), 4,4-bis(4-hydroxyphenyl)-valeric acid (0.01 mol), 5,5-carbonylbis(2-fluorobenzene-sulfonate) (0.002 mol), 4,4′-difluoro benzophenone (0.008 mol), toluene (40 g), and K_2CO_3 (0.25 mol) were added to a 250 mL three-necked round bottom flask that was equipped with a Dean–Stark trap and a nitrogen inlet. The mixture was continuously stirred at room temperature for 12 h. The temperature was then raised to 145 °C and the mixture was refluxed for 4 h. Subsequently, the reaction mixture was heated to 150 °C and refluxed for 10 h in order to remove water through azeotropic distillation. The temperature was then raised to 165 °C (24 h) until the polymer precipitated from the solution. The mixture was cooled to room temperature and the precipitate was dissolved in 20 mL of THF and 5 mL of concentrated HCl. The polymer solution was then filtered, and the precipitate was well washed twice with 500 mL of isopropanol. The solid was washed with deionized (DI) water until the washed fluid showed a pH ~7 and was then dried at 60 °C for 24 h under vacuum to obtain a 90% yield. The relationships between DS and the feed ratio of monomers are listed in Table 1. DS was defined as the average number of sulfonic acid groups per repeating unit of the polymeric materials and was calculated from equation (1).

$$DS = \frac{\text{molar number of } SO_3H \text{ group}}{\text{molar number of the PEEK} - SO_3H \text{ unit} + \text{molar number of the PEEK unit}} \quad (1)$$

DC was defined as the mole percent of cross-linker (BDSA) per repeating unit of CSPAEK polymers and was calculated according to equation (2).

$$DS = \frac{\text{molar number of BDSA} - Na}{\text{molar number of the PEEK} - SO_3H \text{ unit} + \text{molar number of the PEEK unit}} \quad (2)$$

The synthesis procedure of SPAEK with different DS values is illustrated in Scheme 1. FT-IR (Kbr, cm^{-1}) 1026, 1084, 1240 (O=S=O); 1722 (C=O), 2982, 2970 (CH$_2$).

^{1}H NMR (DMSO-d6, ppm) 1, 7.05; 2, 7.72; 3, 8.18; 4, 7.05; 5, 7.26; 6, 7.04; 7, 7.75; 8, 1.59; 9, 1.90; 10, 2.49; 11, 12.04.

2.3. Preparation of activated SPAEK-NHS intermediates

A series of activated SPAEK-NHS intermediates was synthesized, as shown in Scheme 2. In this step, all of the carboxylic acid groups of SPAEK were converted to NHS esters. For the preparation of SPAEK20-NHS, for example, 5.05 g (0.01 mol) SPAEK20, 1.38 g (0.012 mol) NHS, and 2.47 g (0.12 mol) DCC were dissolved in 50 mL dry DMF. The mixture was stirred at room temperature for 12 h, and then heated to 40 °C for 12 h under continuous stirring. The reaction mixture was cooled and filtered to remove the suspended solid. The polymer was then precipitated by dropping the solution slowly into 500 mL of isopropanol under continuous stirring with a magnetic stir bar. After stirring for 5 h, the polymeric product was washed several times with isopropanol and methanol. The final activated SPAEK-NHS products were obtained with a maximum yield of about 95% after drying at 40 °C under reduced pressure for 24 h.

^{1}H NMR (DMSO-d6, ppm) 1, 7.05; 2, 7.72; 3, 8.18; 4, 7.05; 5, 7.26; 6, 7.04; 7, 7.75; 8, 1.59; 9, 1.90; 10, 2.49; 11, 2.77.

2.4. Preparation of CSPAEK membranes

BDSA—Na was obtained in the neutralization of BDSA with NaOH at the mole ratio of 1:2. The membranes were prepared under stirring by dissolving 0.4 g of the activated SPAEK-NHS polymer in 5 mL of DMAc, and mixing with different amounts of BDSA—Na and sodium sulfanilate in 5 mL DMSO. The mixture was cast on glass slides. The polymer was cross-linked at 85 °C for 12 h

in a vacuum oven. The cured film was dried at 85 °C for 24 h under vacuum and then peeled off from the substrate. The freestanding film was immersed in a 1.5 M HCl aqueous solution at room temperature for 12 h and boiled in DI water to remove the excess of HCl and NHS. This washing procedure was repeated until the pH of the washed water reached ~7. The CSPAEK membranes were then stored in DI water at room temperature until further use. The resulting brown-colored membranes were transparent, tough, flexible and homogeneous. The thickness of the CSPAEK membrane was 160—180 μm. The synthesis procedure of the CSPAEK membranes with different DS values is shown in Scheme 2.
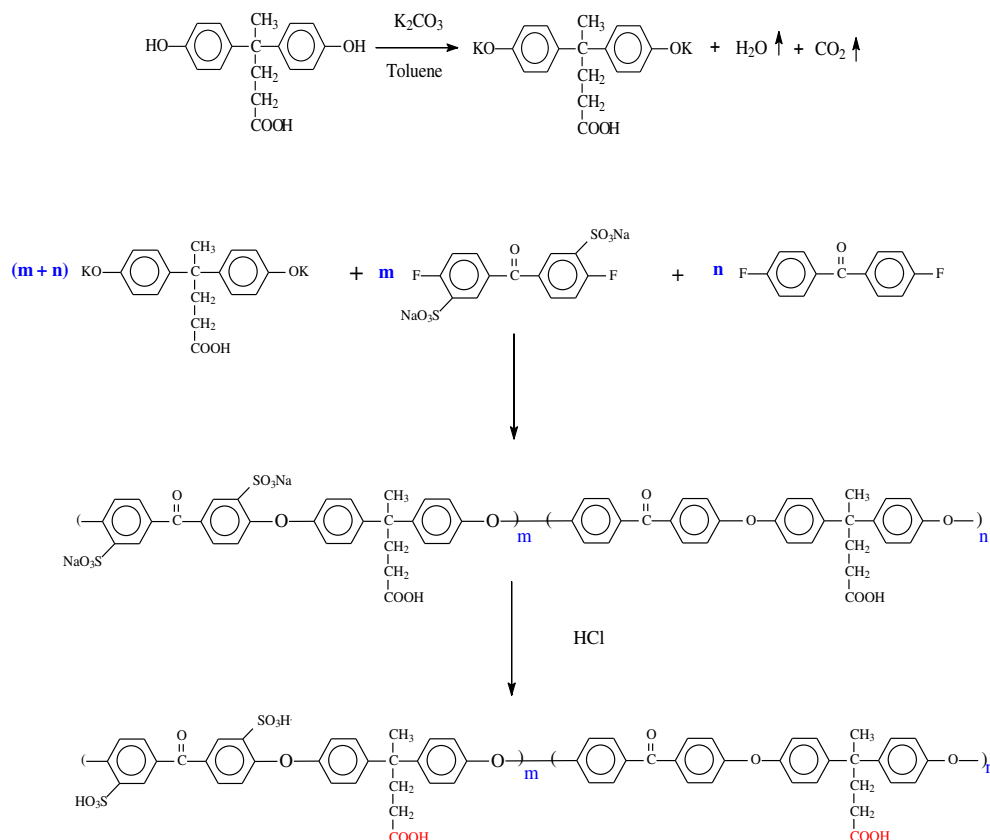
2.5. Characterization

2.5.1. Chemical identification

The chemical structure of the CSPAEK membranes was confirmed using attenuated total reflection (ATR − FT-IR) (Bruker IFS 66/S, Bruker, Germany). The infrared radiation range was from 4000 to 500 cm^{-1}, and the scan time to obtain the spectrum was about 32 s with a resolution of 4 cm^{-1}.
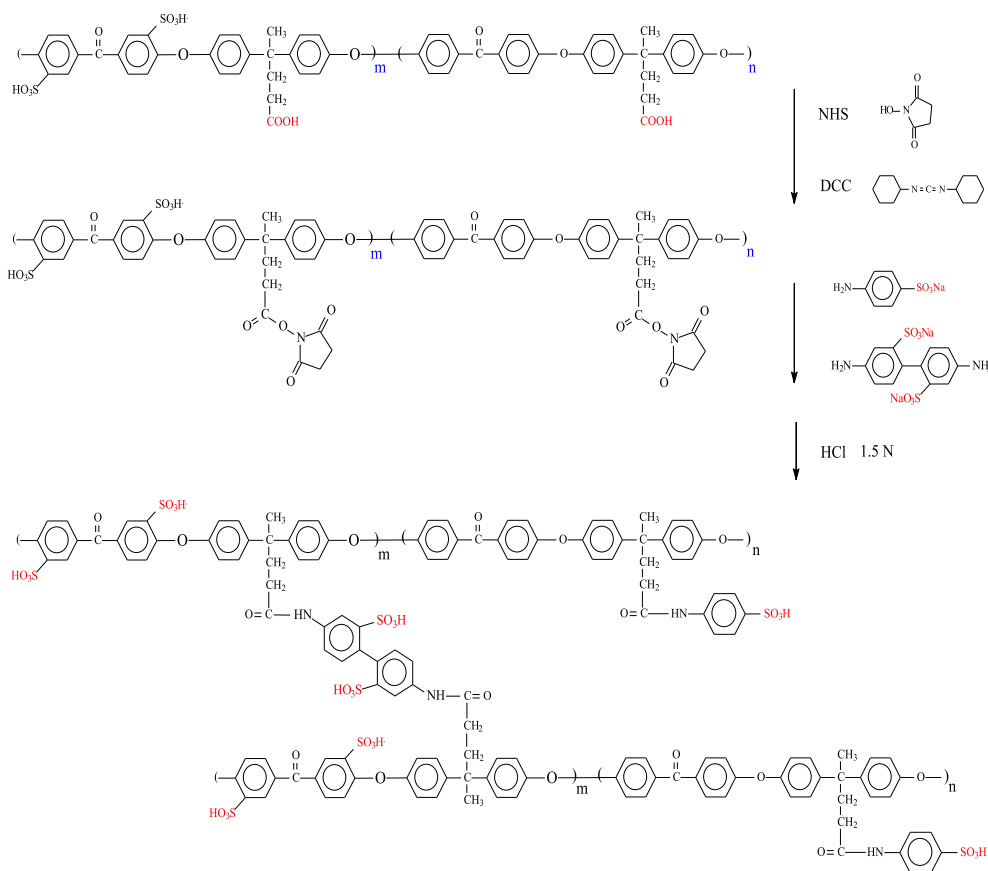
^{1}H NMR (Ed- this acronym has already been defined above) spectra were recorded using a Varian Unity INOVA 500 MHz NMR spectrometer (Varian, USA) at room temperature. DMSO-d6 was used as the solvent, and tetramethylsilane as the internal standard.

2.5.2. Proton conductivity

The proton conductivity of the membrane samples was measured by alternating current (AC) impedance spectroscopy using a Zahner IM6e impedance unit (Zahner, Germany) and a BEKKTECH (Bekktech, USA) cell, where the AC frequency was scanned from 1 MHz to 1 Hz at 5 mV. The samples were kept at

Scheme 1. Synthetic pathway of SPEAK containing the pedant carboxylic acid groups.

Scheme 2. Synthetic pathway of CSPAEK.

room temperature for approximately 30 min at 90% relative humidity before taking the measurements. The bulk resistance (R) for all the samples was obtained from the impedance spectroscopy plot. The ionic conductivity (σ) was calculated using the following equation:

$$\sigma = \frac{L}{R \cdot W \cdot l} \tag{3}$$

where σ is the proton conductivity (S cm^{-1}), L is the length parallel to the ion flow (cm), and W and l are the width (cm) and thickness (cm) of the electrolyte membrane, respectively.

2.5.3. Thermal properties

A thermogravimetric analyzer (TGA2050, TA Instruments, USA) was used to investigate the thermal degradation behavior of the CSPAEK samples. The samples were heated from room temperature to 700 °C at a scanning rate of 10 °C min^{-1} in nitrogen atmosphere.

2.5.4. Methanol permeability

All samples were stored in DI water before testing. Methanol permeability was determined using a diaphragm diffusion cell. The glass cell consists of two identical compartments containing 2 M methanol on one side and DI water on the other side, and the test membrane was clamped between the two compartments. Both compartments were kept stirred using magnetic bars during the permeation experiments. The concentration of methanol in the permeate stream was measured by a refractive index detector (RI750F Younglin Instrument, Anyang, Korea). The methanol permeability (P) was then calculated from the slope of the linear plot of the methanol concentrations vs. permeation time, according to the following relationship:

$$C_b = \frac{A}{V_b} \frac{DK}{l} C_a(t - t_0) \tag{4}$$

where C_a and C_b are the methanol concentrations in the feed and permeated sites, respectively, t_0 is the time flag, A the area of membrane, l is the thickness of membrane, and D and K are the methanol diffusion coefficient and partition coefficient between the membrane and adjacent solution, respectively.

2.5.5. Water uptake

The water uptake expressed in wt% was determined by measuring the weight differences between the fully dried and the fully hydrated membranes. Before the water uptake measurement, the membranes were dried in a vacuum oven at 90 °C for 24 h in order to determine their dry weights (W_d). The dried membranes were then immersed in DI water at various temperatures for 24 h to attain equilibrium state of water uptake. The sample was wiped to remove any water on the surface and then weighed (W_w). This process was repeated several times until a constant weight was attained. The water uptake of the membranes was calculated using the following equation:

$$\text{water uptake} = \frac{W_w - W_d}{W_d} \times 100\% \tag{5}$$

2.5.6. Mechanical strength

The tensile strength of both non-cross-linked and cross-linked membranes was measured using a universal tensile machine (UTM model 5565, Lloyd, Fareham, UK). The samples were placed in water at 40 °C to imbibe water up to equilibrium. The surface of the wet samples was blotted dry with a tissue before the sample was
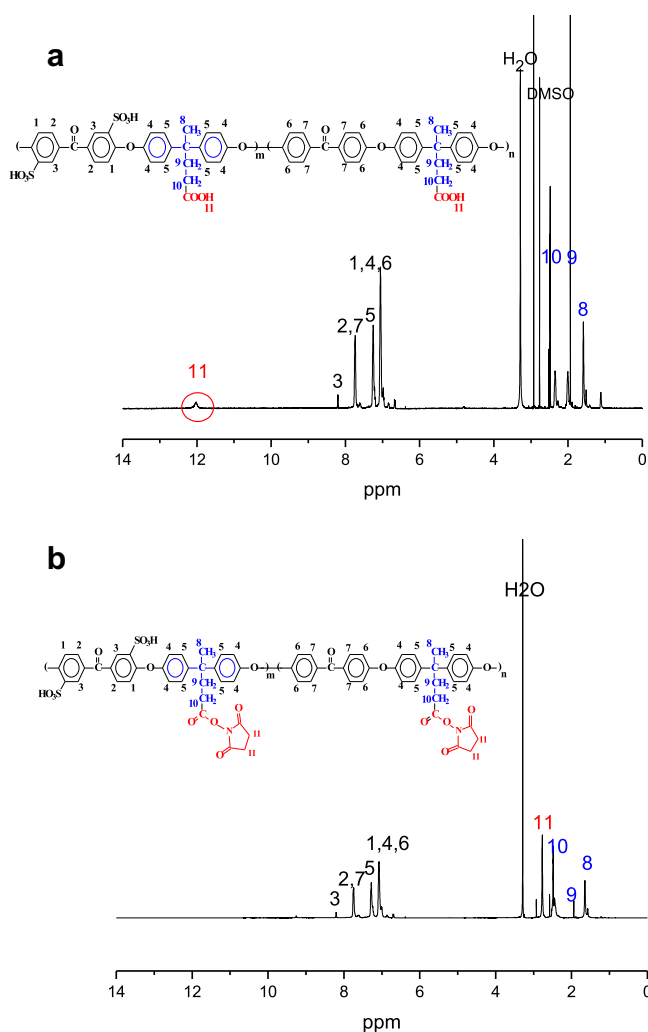
Fig. 1. ^{1}H NMR spectra of (a) SPAEK containing the pendant carboxylic acid groups and (b) activated SPAEK-NHS intermediate, respectively.

3. Results and discussion

3.1. Synthesis of SPAEK

The chemical structure of the synthesized SPAEKs was identified by ^{1}H NMR. As shown in Fig. 1a, the ^{1}H NMR spectrum of the SPAEK20 polymer sample was completely assigned. The signals of the ortho-, meta-, and para-protons in the benzene group were observed at 8.1, 7.7, and 7.3 ppm, respectively. The proton signals of the carboxylic group were displayed at 12 ppm in the SPAEK sample, but totally disappeared in the synthesized SPAEK-NHS sample, as shown in Fig. 1b, apparently due to the conversion of the free carboxylic acid group to the NHS-activated acid group. Additionally, the NHS proton signal that was observed at 2.78 ppm strongly suggested that the reaction of SPAEK with NHS was successfully performed to produce an NHS-activated SPAEK intermediate.

The backbone (aryl group) SPAEK was obtained from the direct polymerization of the sulfonated monomers. FT-IR spectroscopy was used to confirm the presence of sulfonated groups in PAEK. In Fig. 2a, the FT-IR spectrum of SPAEK25 (with 25% DS on the backbone, but before cross-linking) shows the characteristic symmetrical and asymmetrical stretching of the SO_3H group at 1240, 1011,

loaded for mechanical test. The samples were 20 mm wide and extension rate was 50 mm min^{-1} within 21 cm of Gauge length. The measurements were conducted at least three times and the average value was taken for its determination.

2.5.7. SAXS analysis

The small angle X-ray scattering (SAXS) technique was used to investigate the radical structure of the particles and the average ionic cluster dimension of the membranes. The CSPAEK membrane was first immersed in a 1.0 M CsCl solution for 24 h to exchange the protons of the sulfonic groups with the ionic cesium. The membrane was then washed with DI water before measurement. All SAXS experiments were carried out using Synchrotron radiation with $\lambda=1.608$ Å at the 4C1 lines at Seoul National University. The average diameter of the ionic clusters in the CSPAEK membranes was calculated by the following formula:

$$d = \frac{2\pi}{q} \tag{6}$$

where d is the average ion cluster dimension of the membrane (Å) and q is the scattering vector (Å).
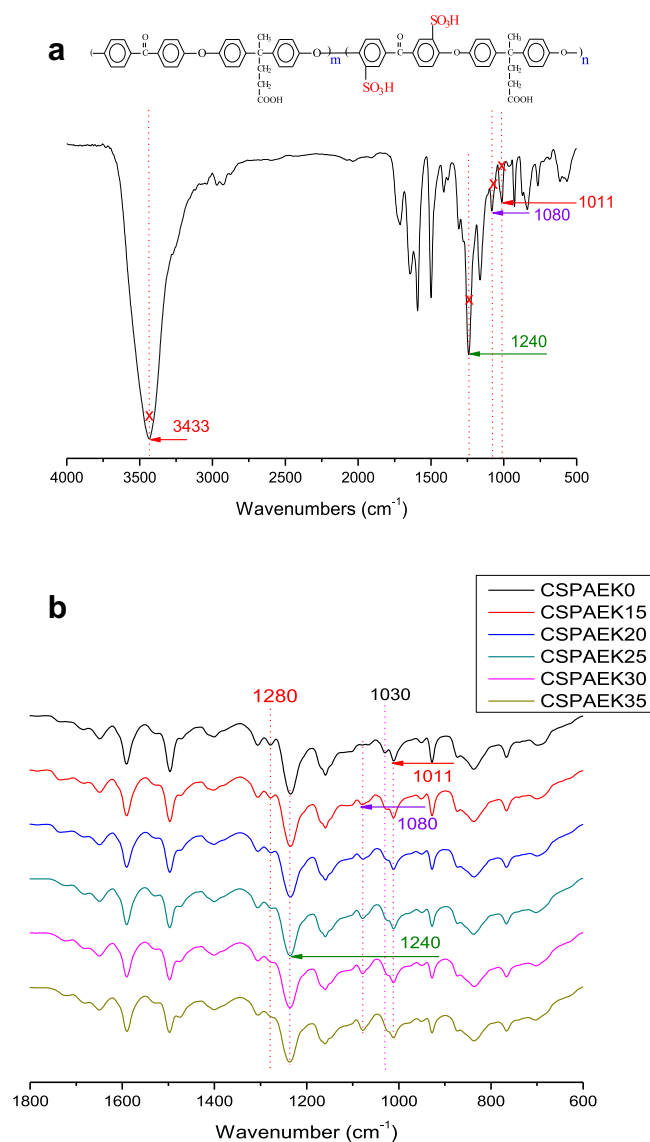
Fig. 2. FT-IR of (a) SPAEK20 and (b) CSPAEK with different sulfonation degrees.
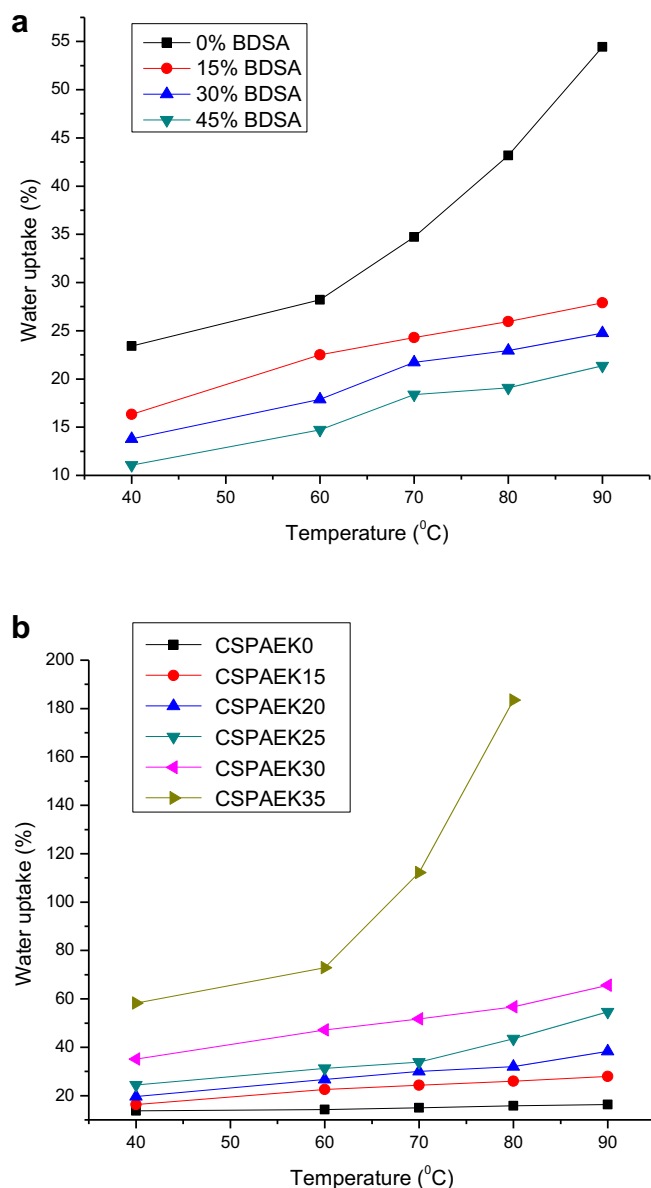
Fig. 3. Water uptake of (a) CSPAEK15 membranes with different cross-linking degrees at different temperatures and (b) CSPAEK and Nafion 117 membranes with different sulfonation degrees at different temperatures.
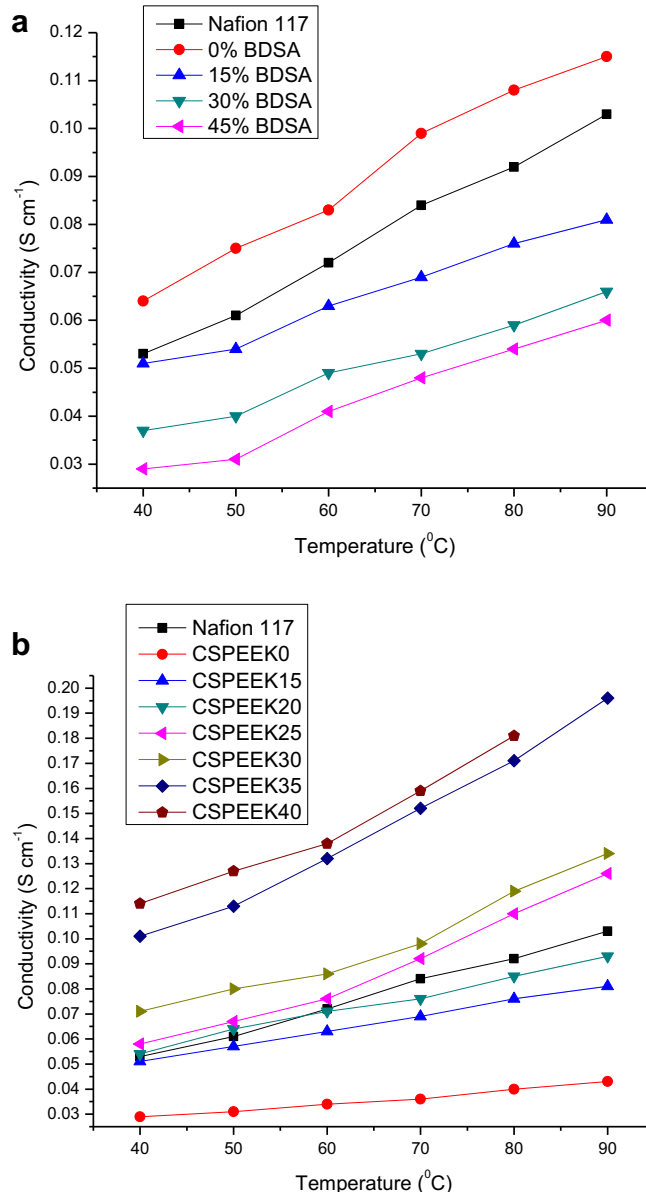

Fig. 4. Temperature dependence of proton conductivity of (a) CSPAEK membranes with different cross-linking degrees and (b) CSPAEK and Nafion 117 membranes with different sulfonation degrees.

1080 and 3433 cm^{-1}. More specifically, the broad band at ~3433 cm^{-1} was assigned to the O–H vibration of SO$_3$H as well as to the absorbed moisture. The other bands were due to vibrations associated with O=S=O stretch (~1240 cm^{-1}), symmetric O=S= O stretch (~1080 cm^{-1}), and S=O stretch (1011 cm^{-1}) [45]. The chemical composition of the CSPAEK membranes with different DS values was also investigated by FT-IR spectroscopy. Fig. 2b displays the FT-IR spectra of the CSPAEK membranes (after cross-linking) in the wave number ranging from 1800 to 600 cm^{-1} The peak intensity at 1080 cm^{-1} (O=S=O stretch) and 1011 cm^{-1} (S=O stretch) clearly increased with increasing DS. These FI-IR and NMR spectra thus provide strong experimental evidence for the successful synthesis of the CSPAEK membranes.

3.2. Water uptake

The water uptake of the membrane is very important in fuel cell application. Basically, absorbed water can facilitate proton

transport in the membranes. However, excessively high water uptake may lead to problems of poor dimensional stability and mechanical deterioration under long-term operation. The water uptake of the prepared membranes with different cross-linking densities is shown in Fig. 3a. As expected, the water uptake decreased with increasing cross-linking density. The membranes with the highest cross-linking density, 45% in this series, had a water uptake of 21.37% at 90 °C, compared to 54.43% for those at the lowest cross-linking density at the same temperature. The water uptake of the cross-linked membranes was greatly reduced compared with that of the uncross-linked membranes. However, an excessively high cross-linking density makes the molecular structure of the membrane so tight that the proton conductivity may be greatly reduced in a brittle state, as shown in Fig. 4a. For this reason, the CSPAEK membranes with a cross-linking percentage above 15% were not selected for further study.

Fig. 3b shows the water uptake of the CSPAEK membranes with different DS values at 15% cross-linking density. The water uptake

of the CSPAEK membrane increased with increasing DS. CSPAEK0 (no backbone sulfonated) exhibited a water uptake of 16.34% at 90 °C, but CSPAEK35 was partially soluble in water at the same temperature. Clearly, the CSPAEK35 membrane is not suitable for fuel cell applications.

3.3. Proton conductivity

High proton conductivity is a prerequisite for good fuel cell performance. The effect of the cross-linking density on the proton conductivity of the CSPAEK15 membrane (CSPAEK with a fixed backbone DS of 15%) is shown in Fig. 4a. The effect of DS on the proton conductivity of CSPAEK with a fixed DC of 15% is also illustrated in Fig. 4b. The proton conductivity increases considerably with increasing temperature. In Fig. 4a, the conductivity is decreased with increasing cross-linking density of the membrane, as the molecular mobility of the polymer lessens with increasing DC. However, this cross-linking density effect on the proton conductivity was not as strong as the DS effect, as the sulfonic acid groups were attached on the cross-linker in this study to minimize such a negative effect. The uncross-linked membrane showed a very high conductivity of 0.115 S cm^{-1} at 90 °C, which was higher than that of Nafion® under the same condition. However, the proton conductivity of the cross-linked membranes was lower than that of Nafion® 117.

In Fig. 4b, the proton conductivity of the CSAPEK membranes increases with increasing DS and temperature. The conductivity was increased from 0.029 S cm^{-1} to 0.101 S cm^{-1} with increasing DS from 100% (CSPAEK0) to 135% (CSPAEK35) at 40 °C, whereas it was increased from 0.043 S cm^{-1} to 0.196 S cm^{-1} at 90 °C. For the CSPAEK0 membrane, the proton conductivity was increased from 0.029 S cm^{-1} to 0.043 S cm^{-1} with increasing temperature from 40 °C to 90 °C, which was much lower than that of Nafion® 117. Among the membranes carrying sulfonic acid groups on their aromatic backbone, the CSPAEK25 membrane showed a higher conductivity than that of Nafion® over the whole temperature range. Although the CSPAEK40 membrane, that with the highest DS, showed the highest proton conductivity of 0.181 S cm^{-1} at 80 °C, this membrane was not suitable for actual applications as it was cracked in water due to excessive high swelling at 90 °C. The cross-linking density of the membranes was fixed at 15% for this study of the DS effect on the proton conductivity, considering the relatively low water uptakes and high proton conductivities that are shown in Figs. 3a and 4a.

3.4. Thermal properties

The degradation process and thermal stability of the CSPAEK membranes were investigated using thermogravimetric analysis (TGA) in Fig. 5. A weight loss of about 5% was recorded in the temperature range from 150 °C to 250 °C due to the evolution of the water from the membranes. This weight loss increased with increasing DS, implying that the dried samples with a higher DS absorbed more water because of their higher hydrophilicity. The weight loss between 260 and 290 °C was associated with the decomposition of sulfonic acid groups. The third weight loss, of about 25%, around 450 °C, was due to the decomposition of the polymer main chains. CSPAEK35, the membrane with the highest DS among the 3 tested samples, exhibited the largest weight loss of 50% because the amount of decomposed sulfonic acids was the highest. The thermal stability of the CSPAEK membranes studied in this research is high enough for the membranes to serve as a PEM in fuel cell applications.
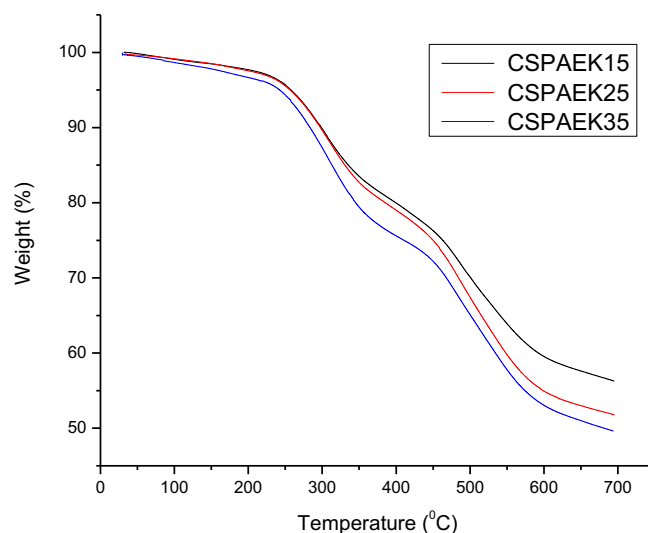

Fig. 5. TGA results of CSPAEK membranes.

3.5. Methanol permeability and selectivity

Prior to the methanol permeability measurements, all the CSPAEK membrane samples were soaked for 24 h in DI water to full hydration. In general, the methanol crossover not only reduces fuel efficiency but decreases the cathode performance. In Fig. 6, the methanol permeability was investigated as a function of the DS of the CSPAEK membranes. All the membranes exhibited low methanol permeability in comparison with Nafion® 117. More specifically, the methanol permeability increased with increasing DS from 4×10^{-7} to 10.3×10^{-7} cm^2 s^{-1} for CSPAEK15 to CSPAEK35, respectively. The trend of these results was in good agreement with the water uptake shown in Fig. 3b.

Technically, PEMs with high proton conductivity and low methanol crossover are desirable for achieving efficient fuel cell performance. The proton transfer selectivity of the membranes is determined by the combined effects of proton conductivity and methanol crossover. More specifically, the selectivity is defined as the ratio of proton conductivity to methanol permeability. As shown in Fig. 7, all the CSPAEK membranes exhibited higher
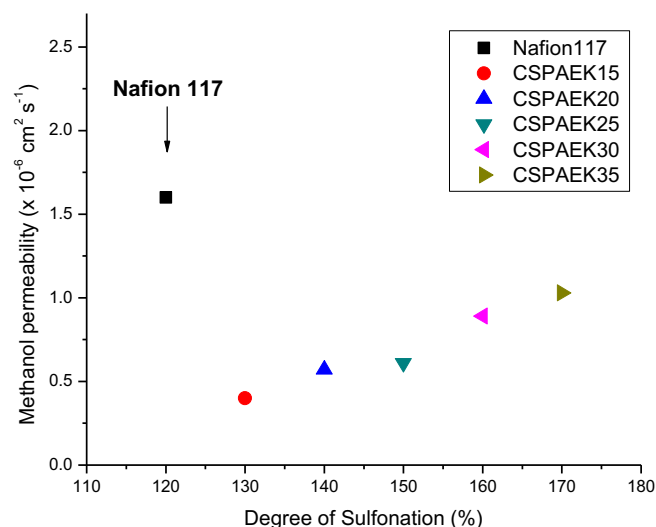

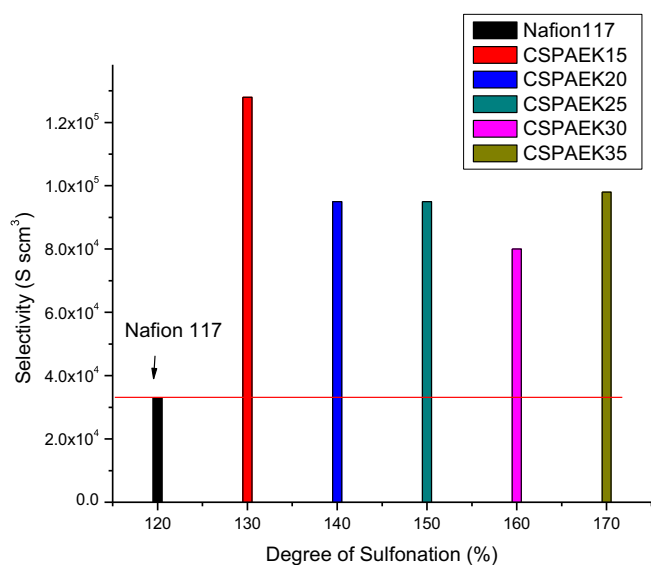**Fig. 6.** Methanol permeability of CSPAEK and Nafion 117 membranes.

Fig. 7. Selectivity of CSPAEK and Nafion 117 membranes.

selectivity than Nafion® 117. The CSPAEK15 membrane exhibited the highest selectivity among the three tested membranes.

3.6. Mechanical strength

The mechanical strength and toughness of the membrane are very important to long-term fuel cell performance. In this study, the mechanical properties of the fully hydrated membrane were investigated. The mechanical properties of Nafion® and the CSPAEK membranes are shown in Fig. 8. Generally, the CSPAEK membrane with 15% cross-linking density showed a higher tensile strength than that of Nafion 117. The membranes with low DSs exhibited good flexibility and toughness compared to Nafion®. For example, CSPAEK15 showed high strain (107%) and high maximum stress at break (18.7 Mpa). However, the high water uptake of the CSPAEK35 membrane limited its mechanical strength [46]. Among these three membranes, CSPAEK35 with the highest DS showed the lowest tensile strength as expected.
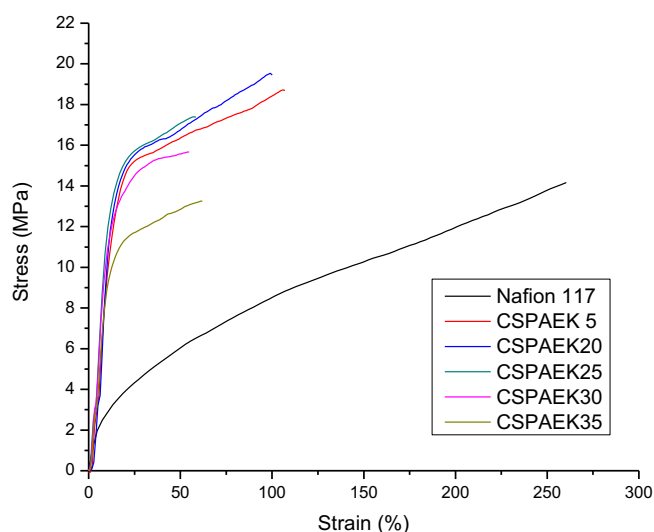

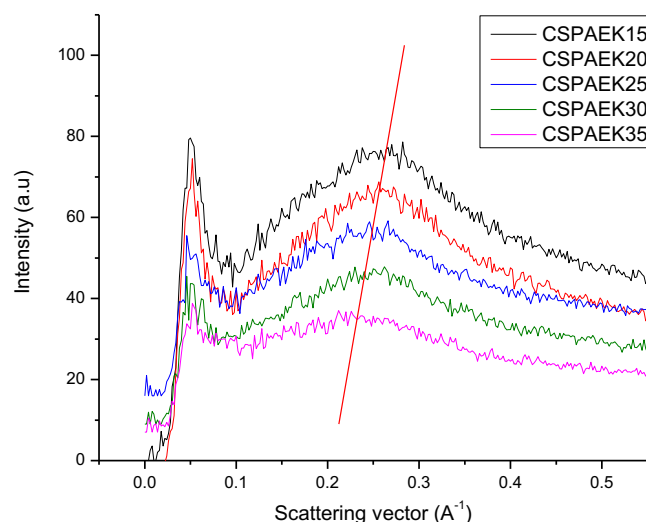**Fig. 8.** Mechanical stability of CSPAEK and Nafion 117 membranes.

Fig. 9. SAXS patterns of the CSPAEK membranes.

Table 2
Scattering vector and ionic cluster dimension of CSPAEK membranes.

Sample	DS (%)	Scattering vector q (Å)	Ionic cluster dimension d (nm)
CSPAEK15	170	0.264	2.38
CSPAEK20	190	0.260	2.42
CSPAEK25	200	0.256	2.45
CSPAEK30	210	0.251	2.50
CSPAEK35	220	0.230	2.73

3.7. SAXS analysis

The morphology of the CSPAEK membranes with different DS values was studied extensively by SAXS. The CSPAEK membranes were first treated by soaking in 1 M CsCl solution for 24 h, and then washed with DI water prior to measurement. The SAXS profiles of the CSPAEK membranes are shown in Fig. 9. In Table 2, the length of scattering vector q in the SAXS experiment range from 2.23 to 2.65 nm, indicating that the dimension of the ionic clusters increase with increasing DS. The results strongly confirmed the experimental data revealing that the proton conductivity was enhanced with increasing DS.

4. Conclusions

A successfully prepared series of CSPAEK membranes exhibit excellent proton conductivities that are higher than that of the Nafion 117 membrane. Moreover, the proton conductivity can be controlled precisely by varying the feed ratios of sulfonated to unsulfonated monomers. The proton conductivity of the CSPAEK membranes increases with increasing DS and temperature. All CSPAEK membranes exhibit excellent thermal and mechanical stability and low methanol permeability. The selectivity of all the investigated membranes is higher than that of the Nafion membrane. Among all CSPAEK membranes in this study, the CSPAEK15 membrane, with 15% cross-linking density and 115% DS, exhibits the highest selectivity along with excellent mechanical and thermal stability. To summarize, the overall experimental results support the CSPAEK15 membrane as a promising potential alternative to Nafion® 117.

Acknowledgements

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